

## 176 Carbon, Graphite, Diamond, and Fullerenes

Of the two fibers, only the wet-spun PAN is used as precursor. It contains a co-polymer, such as itaconic acid or other proprietary compounds, that apparently catalyzes the cyclization in air and helps the carbonization process.<sup>[1]</sup> The dry-spun fiber is not as suitable and is not used.

**Stretching.** The spun fiber is composed of a fibrillar or ribbon-like network, which acquires a preferred orientation parallel to the fiber axis, providing that the fiber is stretched either while it is still in the coagulating bath, or subsequently in boiling water, as shown in Fig. 8.4. This stretching results in an elongation of 500 to 1300%, and is an essential step to obtain a high-strength fiber.

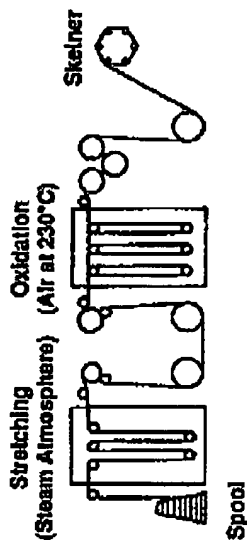


Figure 8.4. Schematic of stretching and oxidation steps in the production of PAN-based carbon fibers.<sup>[1]</sup>

**Stabilization and Oxidation.** During the carbonization process, the elimination of the non-carbon elements (hydrogen and nitrogen) is usually accompanied by chain scission and relaxation of the fibrillar structure. This is detrimental to the formation of high-strength and high-modulus fibers, but can be avoided by a stabilization process prior to carbonization.

This stabilization consists of slowly heating the stretched fiber to 200–280°C in an oxygen atmosphere (usually air) under tension to maintain the orientation of the polymer/skeleton and stabilize the structure (Fig. 8.4). The addition of ammonia to oxygen increases the rate of stabilization.<sup>[14]</sup>

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The molecular changes occurring during stabilization are shown in Fig. 8.5.<sup>[11]</sup> The oxidation causes the formation of C=C bonds and the incorporation of hydroxyl (-OH) and carbonyl (-CO) groups in the structure. These factors promote cross-linking and thermal stabilization of the fiber which, at this stage, can no longer melt. This non-meltable characteristic is essential to prevent the filaments from fusing together.

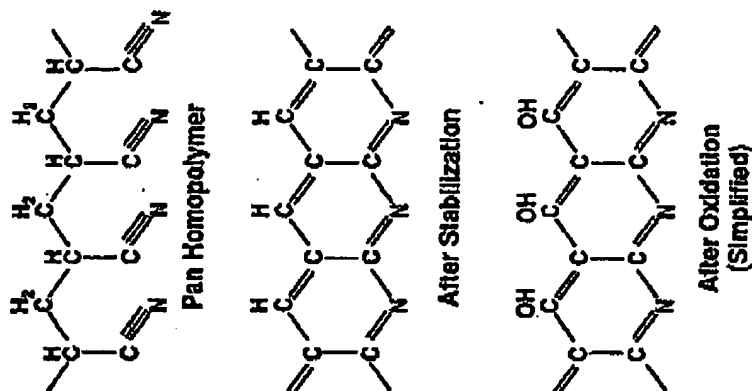


Figure 8.5. Molecular changes in PAN after stabilization and oxidation.<sup>[11]</sup>

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**Carbonization and Graphitization.** Carbonization takes place between 1000 and 1500°C. These temperatures are reached slowly, at a heating rate of ~20°C/min. During this stage a considerable amount of volatile by-products is released. These include H<sub>2</sub>O, CO<sub>2</sub>, CO, NH<sub>3</sub>, HCN, CH<sub>4</sub>, and other hydrocarbons. The carbon yield is between 50 and 55%. The circular morphology of the fiber is maintained and the final diameter varies from 5 to 10 µm, which is approximately half that of the precursor PAN fiber. The removal of nitrogen occurs gradually over a range of temperatures as shown below:<sup>[11]</sup>

600°C	- nitrogen evolution starts
900°C	- maximum evolution
1000°C	- 6% nitrogen left
1300°C	- 0.3% nitrogen left

The tensile modulus of the fiber can be further increased by graphitization. It can be argued that the term "graphitization" is not correct since a true graphite structure is not obtained, and "high-temperature heat-treatment" would be a better term. This heat-treatment is usually carried out at temperatures up to 2500°C. The final carbon content is greater than 99%.

## 2.3 Structure of PAN-based Carbon Fibers

**Analytical Techniques.** Analytical techniques to determine the structure of carbon fibers include: wide-angle and small-angle x-ray diffraction, electron diffraction, neutron scattering, Raman spectroscopy, electron microscopy, and optical microscopy. Detailed reviews of these techniques are found in the literature.<sup>[14]</sup>

**Structure.** The structure of PAN-based carbon fibers is still conjectural to some degree. Yet, thanks to the recent advances in analytical techniques just mentioned, an accurate picture is beginning to emerge.

Unlike the well-ordered parallel planes of pyrolytic graphite which closely match the structure of the graphite crystal, the structure of PAN-based carbon fibers is essentially turbostratic and is composed of small two-dimensional fibrils or ribbons. These are already present in the precursor and are preferentially aligned parallel to the axis of the fiber. The structure may also include lamellae (small, flat plates) and is probably a combination of both fibrils and lamellae.<sup>[15,16]</sup>

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**Crystallite Size.** Several structural models have been proposed including the one shown in Fig. 8.6.<sup>[11]</sup> The critical parameters (as determined by x-ray diffraction) are  $L_c$ , which represents the stack height of the ribbon and the crystallite size  $L_a$ , which in this case can be considered as the mean length of a straight section of the fibril.<sup>[11]</sup> This alignment ( $L_a$ ) becomes more pronounced after high-temperature heat-treatment which tends to straighten the fibrils. However,  $L_c$  still remains small and is generally less than 20 nm, as shown in Fig. 8.7.<sup>[7]</sup> This figure also shows the much greater increase of crystallite size ( $L_a$ ) of pitch-based fibers (see Sec. 3.0 below).

The straightening of the fibrils occurs preferentially, the outer fibrils being more oriented (straightened) than the inner ones as shown in Fig. 8.8.<sup>[11]</sup> This has an important and favorable consequence, that is, most of the load-bearing capacity is now transferred to the outer portion or "skin" of the fiber.

**Interlayer Spacing.** The change in interlayer spacing ( $c$  spacing) of PAN-based carbon fibers as a function of heat-treatment temperature is shown in Fig. 8.9.<sup>[7]</sup> This spacing never shrinks to less than 0.344 nm, even after a 3000°C heat-treatment, indicating a poor alignment of the basal planes and the presence of defects, stacking faults, and dislocations. This behavior is characteristic of carbons produced from polymers (see Ch. 6). Also shown in Fig. 8.9 is the decrease in interlayer spacing of a pitch-based fiber. It is far more pronounced than that of the PAN-based fiber (see Sec. 3.0 below).

**Sp<sup>2</sup> and Sp<sup>3</sup> Bonding.** Another important structural characteristic of PAN-based fibers is the probable existence of sp<sup>3</sup> hybrid bonding as indicated by Raman spectroscopy and shown in Fig. 8.10. In this figure, the pitch-based graphitized fiber (P 100) is the only one to exhibit a strong sp<sup>2</sup> line. All others show structural disorders which may be caused by some sp<sup>3</sup> bonding.<sup>[7]</sup> The fibers listed in Fig. 8.10 are identified in Secs. 6.3 and 6.4 below.

Both sp<sup>2</sup> and sp<sup>3</sup> hybrid bonds are strong covalent bonds, with the following bond energy and bond lengths (see Ch. 2, Secs. 3 and 4):

sp <sup>2</sup>	- 370 kJ/mol and 0.15 nm
sp <sup>3</sup>	- 680 kJ/mol and 0.13 nm

These strong bonds within the crystallites (or fibrils) and the preferred orientation of these crystallites account, at least in part, for the high stiffness inherent to most carbon fibers.